PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

BASELL POLYOLEFINE GMBH
Intellectual Property - F 206
Carl-Bosch-Str. 38
67056 Ludwigshafen
ALLEMAGNE

Date of mailing *(day/month/year)* 08 July 2004 (08.07.2004)	
Applicant's or agent's file reference LU6083	**IMPORTANT NOTICE**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2003/014650	19 December 2003 (19.12.2003)	20 December 2002 (20.12.2002)

Applicant: BASELL POLYOLEFINE GMBH et al

1. Notice is hereby given that the International Bureau has **communicated**, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this notice:

   AU, AZ, BY, CH, CN, CO, DZ, EP, HU, JP, KG, KP, KR, MD, MK, MZ, RU, TM, US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

   AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BZ, CA, CR, CU, CZ, DE, DK, DM, EA, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, ID, IL, IN, IS, KE, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PG, PH, PL, PT, RO, SC, SD, SE, SG, SK, SL, SY, TJ, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW

   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-*bis*)).

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on 08 July 2004 (08.07.2004) under No. WO 2004/056922

4. **TIME LIMITS for filing a demand for international preliminary examination and for entry into the national phase**

   The applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of **19 months** from the priority date, but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

   In practice, **time limits other than the 30-month time limit** will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For **regular updates on the applicable time limits** (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at http://www.wipo.int/pct/en/index.html.

   For filing a **demand for international preliminary examination**, see the *PCT Applicant's Guide*, Volume I/A, Chapter IX. Only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

   It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.+41 22 740 14 35	Authorized officer Agnes Wittmann-Regis Facsimile No.+41 22 338 89 70

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 July 2004 (08.07.2004)

PCT

(10) International Publication Number
WO 2004/056922 A1

(51) International Patent Classification[7]: **C08L 23/10**, F16L 9/12, C08L 23/12, 23/14, C08F 10/06, 210/06, C08K 5/34

(21) International Application Number: PCT/EP2003/014650

(22) International Filing Date: 19 December 2003 (19.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

102 61 107.6	20 December 2002 (20.12.2002)	DE
60/442,821	27 January 2003 (27.01.2003)	US

(71) Applicant (*for all designated States except US*): **BASELL POLYOLEFINE GMBH** [DE/DE]; Brühler Strasse 60, 50389 Wesseling (DE).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **DOLLE, Volker** [DE/DE]; Wolfsgartenstrasse 27, 64625 Bensheim (DE). **BÖHM, Thomas** [DE/DE]; Händelstrasse 53, 64291 Darmstadt (DE). **TERWYEN, Herbert** [DE/DE]; Niddastrasse 26, 65239 Hochheim (DE).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/056922 A1

(54) Title: MOLDING COMPOSITIONS MADE FROM A HIGH-MOLECULAR-WEIGHT PROPYLENE POLYMER

(57) Abstract: Molding compositions made from a high-molecular-weight propylene polymer with a melt massflow rate MFR of from 0.3 to 1 g/10 min, to ISO 1133 at 230°C and 5 kg, and with a proportion of β modification crystallites in the range from 2 to 20% by weight. The molding compositions of the invention preferably comprise a quinacridone pigment as nucleating agent. The high-molecular-weight propylene polymer used preferably comprises a high-molecular-weight propylene copolymer with up to 30% by weight of other copolymerized olefins having up to 10 carbon atoms. One of the uses of the molding compositions of the invention is as materials for pipes.

Molding compositions made from a high-molecular-weight propylene polymer

The present invention relates to molding compositions made from a high-molecular-weight propylene polymer with a melt mass-flow rate MFR of from 0.3 to 1 g/10 min, to ISO 1133 at 230°C and 5 kg, and with a proportion in the range from 2 to 20% by weight of β modification crystallites.

The present invention further relates to a process for preparing the molding compositions of the invention, to their use as materials for pipes, and also to pipes made from the molding compositions of the invention.

Propylene polymers may be prepared by liquid-phase polymerization, or else by polymerization in the monomer (bulk phase polymerization), or in a suspension (slurry), or by gas-phase polymerization. The polymerization here is carried out with the aid of a Ziegler–Natta catalyst system which is usually composed of a titanium-containing solid component, of an organic aluminum compound, and of an organic silane compound (EP–B 45 977, EP–A 171 200, US-A 4 857 613, US–A 5 288 824). However, propylene polymers may also be obtained with the aid of metallocene compounds, or of metal complexes having polymerization activity.

Examples of products obtained from propylene polymers are moldings, such as pipes, fittings, blow moldings, rods, and sheets.

These industrially useful propylene polymers have an isotactic structure. It is known that isotactic polypropylene can crystallize in a number of crystal modifications. The modification most frequently encountered is the monoclinic α modification. The hexagonal β modification can also occur in various proportions together with the α modification, and the proportion of β modification crystallites can in particular be increased by adding specific nucleating agents (K.H. Moos, B. Tilger, Angewandte Makromolekulare Chemie 94 (1981), pp. 213-225). EP-A 177 961 teaches that polypropylenes with a proportion in the range from 40 to 60% of β modification crystallites can be obtained using the gamma phase of linear trans-quinacridone as nucleating agent, and polypropylenes with a proportion of more than 70% of β modification crystallites are obtained by using mixed crystals of linear trans-quinacridone with quinacridone quinone.

DE–A 40 19 053 discloses propylene homopolymers with broad dispersity. These propylene homopolymers can also be used as materials for pipes. However, the resultant pipes are relatively brittle and have a rough surface, and therefore have no practical use.

EP–A 808 870 moreover describes high-molecular-weight copolymers of propylene with subordinate proportions of ethylene, and these can be processed using conventional production

$$k = \frac{H(300)_\beta}{H(300)_\beta + H(110)_\alpha + H(040)_\alpha + H(130)_\alpha}$$

is preferably used here to determine the k which gives the relative proportion of the crystalline β modification. $H(110)_\alpha$, $H(040)_\alpha$, and $H(130)_\alpha$ signify the height of the three marked peaks (110), (040), and (130) of the α modification, and $H(300)_\beta$ signifies the height of the marked peak (300) of the β modification. If the β modification is absent, the k value is zero, and if only the β modification is present in the material, the k value is 1.

In one embodiment of the present invention, the DSC crystallization onset for the molding composition of the invention to ISO 11357-1 is at a temperature above 122°C, and preferably below 130°C, particularly preferably from 123 to 129°C, most preferably from 123 to 127°C. When the range specified for the DSC crystallization onset is complied with, the resultant molding compositions have particularly advantageous properties.

The molding compositions of the invention also preferably comprise a quinacridone pigment, present in an amount of from 0.001 to 0.5% by weight, in particular from 0.002 to 0.2% by weight, and particularly preferably in an amount of from 0.002 to 0.1% by weight, based on the entire molding composition. It is particularly preferable here for the nucleating agent used to comprise the gamma phase of linear trans-quinacridone, marketed with the trade name PV Echtrot E3B or E5B from Clariant GmbH, Frankfurt.

The molding compositions of the invention may also comprise, inter alia, conventional additives, such as neutralizing agents, stabilizers, lubricants, fillers, or color pigments, in the usual amounts.

The molding compositions of the invention are obtainable by mixing and melting the high-molecular-weight propylene polymer with the quinacridone pigment, in a mixing apparatus at temperatures of from 180 to 320°C, preferably from 200 to 280°C, particularly preferably from 220 to 260°C. Mixing apparatuses which may be used here are in particular extruders or kneaders, particularly preferably twin-screw extruders. In the case of polymers which are in powder form, it is advantageous to premix the polymer with the nucleating agent and with other additives at room temperature in a mixing apparatus.

For reasons of appearance, it can also be advisable to add appropriate suitable color pigments to the molding compositions of the invention, to give these a desired RAL color number.

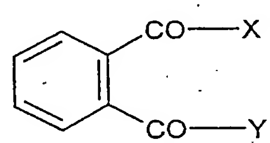
The high-molecular-weight propylene polymer used here can in particular comprise a high-molecular-weight propylene homopolymer, or else a high-molecular weight propylene copolymer with up to 30% by weight of other copolymerized olefins having up to 10 carbon atoms. These other olefins are in particular C_2–C_{10} 1-alkenes, such as ethylene, 1–butene, 1–pentene,

The titanium compounds generally used to prepare the titanium-containing solid component a) generally comprise the halides or alcoholates of tri- or tetravalent titanium, but use may also be made of halogenated titanium alkoxy compounds, or of mixtures of various titanium compounds. It is preferable to use the titanium compounds in which the halogen present is chlorine. Preference is also given to the titanium halides which contain only halogen alongside titanium, and among these particular preference is given to titanium chlorides and especially titanium tetrachloride.

The titanium-containing solid component a) preferably comprises at least one halogen-containing magnesium compound. Halogens here are chlorine, bromine, iodine, or fluorine, preference being given to bromine and in particular to chlorine. The halogen-containing magnesium compounds are either used directly during the preparation of the titanium-containing solid component a) or are formed during preparation thereof. Particularly suitable magnesium compounds for preparing the titanium-containing solid component a) are magnesium halides, in particular magnesium dichloride or magnesium dibromide, or magnesium compounds from which the halides can be obtained in a conventional manner, e.g. via reaction with halogenating agents, examples being magnesium alkyl compounds, magnesium aryl compounds, magnesium alkoxy compounds, and magnesium aryloxy compounds, and Grignard compounds. Preferred examples of halogen-free compounds of magnesium which are suitable for preparing the titanium-containing solid component a) are n–butylethylmagnesium and n–butyloctylmagnesium. Preferred halogenating agents are chlorine or hydrogen chloride. However, the titanium halides may also serve as halogenating agents.

The titanium-containing solid component a) also advantageously comprises electron-donor compounds, for example mono- or polyfunctional carboxylic acids, carboxylic anhydrides, or carboxylic esters, or else ketones, ethers, alcohols, lactones, or organophosphorus or organosilicon compounds.

Preferred electron-donor compounds within the titanium-containing solid component are carboxylic acid derivatives, in particular phthalic acid derivatives of the formula (II)



(II)

where each of X and Y is a chlorine atom or bromine atom or a C_1-C_{10}-alkoxy radical, or X and Y together are oxygen in an anhydride function. Particularly preferred electron-donor compounds are phthalic esters, where X and Y are a C_1-C_8-alkoxy radical. Examples of phthalic esters preferably used are diethyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-pentyl phthalate, di-n-hexyl phthalate, di-n-heptyl phthalate, di-n-octyl phthalate, or di-2-ethylhexyl

analySIS software package.

An example of a method for obtaining the organic oxide whose use is preferred is spray drying of the ground hydrogel, which to this end is mixed with water or with an aliphatic alcohol. These finely-divided inorganic oxides are also available commercially.

The finely-divided inorganic oxide usually also has a pore volume of from 0.1 to 10 cm^3/g, preferably from 1.0 to 4.0 cm^3/g, and a specific surface area of from 10 to 1 000 m^2/g, preferably from 100 to 500 m^2/g, the values here being those determined by mercury porosimetry to DIN 66133 and nitrogen adsorption to DIN 66131.

It is also possible to use an inorganic oxide whose pH, i.e. negative decadic logarithm of proton concentration, is in the range from 1 to 6.5, and in particular in the range from 2 to 6.

Inorganic oxides which may be used are especially the oxides of silicon, of aluminum, of titanium, or of one of the metals of the 1st or 2nd groups of the Periodic Table. A particularly preferred oxide, alongside aluminum oxide, or magnesium oxide, or a phyllosilicate, is silicon oxide (silica gel). It is also possible to use mixed oxides, such as aluminum silicates, or magnesium silicates.

Water is present on the surface of the inorganic oxides used as supports. This water is to some extent bonded physically by adsorption and to some extent chemically in the form of hydroxy groups. The water content of the inorganic oxide can be reduced or entirely eliminated by thermal or chemical treatment, and if this is chemical treatment use is made of conventional drying agents, such as $SiCl_4$, chlorosilanes, or aluminum alkyl compounds. The water content of suitable inorganic oxides is from 0 to 6% by weight. It is preferable to use an inorganic oxide in its commercially available form, without further treatment.

The amounts present of the magnesium compound and of the inorganic oxide within the titanium-containing solid component a) are preferably such that from 0.1 to 1.0 mol, in particular from 0.2 to 0.5 mol, of the compound of magnesium is present per mole of the inorganic oxide.

When preparing the titanium-containing solid component a), use is also generally made of C_1–C_8 alkanols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, n-hexanol, n-heptanol, n-octanol, or 2-ethylhexanol, or a mixture of these. It is preferable to use ethanol.

The titanium-containing solid component may be prepared by methods known per se. Examples of these are given, inter alia, in EP-A 45 975, EP-A 45 977, EP-A 86 473, EP-A 171 200, GB-A 2 111 066, US–A 4 857 613, and US–A 5 288 824. It is preferable to use the process

It is also possible for Ziegler-Natta catalyst systems based on metallocene compounds or based on metal complexes with polymerization activity to be fed into the polymerization reactor in the process for preparing the propylene polymers.

Metallocenes here are complex compounds made from metals of groups 3 to 12 of the Periodic Table with organic ligands, which when combined with metallocenium-ion-forming compounds give effective catalyst systems. For use in the process of the invention, the metallocene complexes are usually present in the catalyst system in supported form. Inorganic oxides are often used as supports. Preference is given to the use of the inorganic oxides described above and also used for preparing the titanium-containing solid component a).

The central atoms present in the metallocenes usually used comprise titanium, zirconium, or hafnium, preferably zirconium. The central atom generally has p-bonding to at least one, generally substituted, cyclopentadienyl group, and also to other substituents. The other substituents may be halogens, hydrogen, or organic radicals, preferably fluorine, chlorine, bromine, or iodine, or a C_1-C_{10}-alkyl group.

Preferred metallocenes contain central atoms having bonding via two p bonds to two substituted cyclopentadienyl groups and particular preference is given to those metallocenes in which substituents of the cyclopentadienyl groups have bonding to both of the cyclopentadienyl groups. Particular preference is given to complexes whose cyclopentadienyl groups also have substitution at two adjacent carbon atoms by cyclic groups.

Other preferred metallocenes are those which contain only one cyclopentadienyl group, which, however, has substitution by a radical which also has bonding to the central atom.

Examples of suitable metallocene compounds are
ethylenebis(indenyl)zirconium dichloride,
ethylenebis(tetrahydroindenyl)zirconium dichloride,
diphenylmethylene-9-fluorenylcyclopentadienylzirconium dichloride,
dimethylsilanediylbis(3-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride,
dimethylsilanediylbis(2-methylindenyl)zirconium dichloride,
dimethylsilanediylbis(2-methylbenzindenyl)zirconium dichloride,
dimethylsilanediylbis(2–methyl–4–phenylindenyl)zirconium dichloride,
dimethylsilanediylbis(2–methyl–4–naphthylindenyl)zirconium dichloride,
dimethylsilanediylbis(2–methyl–4–isopropylindenyl)zirconium dichloride, or
dimethylsilanediylbis(2–methyl–4,6–diisopropylindenyl)zirconium dichloride, and also the corresponding dimethylzirconium compounds.

either to a liquid-phase reactor or via a work-up reactor (flash vessel) finally to a gas-phase reactor.

If a gas-phase reactor is used, the second stage takes place at a pressure of from 10 to 14 bar, at from 30 to 110°C, and with a residence time of from 0.5 to 6 h. Here again, hydrogen can be fed in to regulate the molar mass. If the second stage is likewise carried out in a liquid phase, the polymerization conditions differ from those of the first stage. Another α-olefin, in particular ethylene or 1-butene, can be copolymerized concomitantly here, in particular in the first polymerization stage.

The advantageous embodiments of the invention mentioned may be used advantageously in combination, or else independently of one another. This also in particular applies to the range mentioned for DSC crystallization onset, which provides molding compositions with improved property profile, irrespective of the proportion of the β modification.

The molding compositions of the invention are suitable materials for films, fibers, or moldings, especially as materials for pipes. Their high toughness gives them very good processing properties during the extrusion of pipes whose external diameter d_a is 500 mm or more and whose wall thickness s is greater than or equal to 28.4 mm. Properties of the pipes produced from the molding compositions of the invention are, inter alia, very smooth internal surface, very good results in the long-term internal-hydrostatic-pressure test, and also for circularity and bore-thickness distributions, while the material continues to have high impact strength. In particular, the pipes produced fully comply with the requirements of DIN 8077 in relation to dimensional limits for the average external diameter and ovalities, and the dimensional limits for wall thicknesses.

Compared with pipes with high β content, a particular feature of pipes made from the molding composition of the invention is higher ring stiffness and better dimensional stability.

Examples

The melt mass-flow rates (MFR values) in all of the examples were determined to ISO 1133 at 230°C under a load of 5.0 kg. The ethylene content was determined by infrared spectroscopy, and the polydispersity Mw/Mn by gel permeation chromatography.

The extrapolated crystallization onset temperatures (T_{eiC}, Onset) were obtained from DSC as in DIN EN ISO 11357-1, by extrapolating the baseline and the rising flank of the crystallization peak. A Mettler Toledo STAR machine was used with a cooling rate of 10 K/min for the DSC plot. An average of three measured values was always taken.

Example 3 (inventive):

Injection molding was used to produce tensile specimens from the pellets from example 2. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured was s = 1238 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 18.9 kJ/m^2. Both tests were carried out at 23°C.

Plaques of thickness 1 mm were pressed from the pellets, and subjected to X-ray analysis to determine the proportion of the β modification. The peak heights gave a proportion of 6% of β modification.

Example 4 (inventive):

The pellets from example 2 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 45.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently, and the inner surface of the pipe was very smooth. The pipes had a satisfactory circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.3 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 46.4 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 47.5 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 48.1 mm

Example 6 (comparative example):

Injection molding was used to produce tensile specimens from the pellets from example 5. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured was s = 1342 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 8.9 kJ/m^2. Both tests were carried out at 23°C.

Plaques of thickness 1 mm were pressed from the pellets, and subjected to X-ray analysis to determine the proportion of the β modification. No detectable content of β modification was found.

Example 7 (comparative example):

The pellets from example 5 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 45.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently. The pipes had a circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.8 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 47.2 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 48.6 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 49.1 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 48.3 mm

fed continuously into the reactor. After 48 minutes, 29 Nl of hydrogen were also added. The temperature was held constant at 70°C for 36 minutes. The reactor contents were then worked up by depressurization, meaning that the unreacted propylene was removed by evaporation.

This gave 13.6 kg of a propylene copolymer with 0.5% by weight of copolymerized ethylene. The catalyst yield calculated from these data is 29.5 kg of propylene copolymer/g of catalyst, i.e. titanium-containing solid component. The resultant propylene copolymer had a melt flow rate MFR of 0.90 g/10 min, a cold-xylene-soluble fraction of 4.0% by weight, and a polydispersity Mw/Mn of 10.3. The experiment was repeated a number of times in order to prepare a total amount of 500 kg.

Example 9 (comparative example):

The powder obtained from example 8 was pelletized at about 240°C under an inert gas in a twin-screw extruder with a screw diameter of 53 mm. Stabilizers added here were 0.15% of Irganox® 1010 and 0.15% of Hostanox® PAR 24. Color pigments were also added in order to adjust the color to RAL 7032. 0.2% of ultrafine talc (product commercially available from Luzenac) was added as nucleating agent. The MFR 230/5 measured on the pellets was 1.04 g/10 min. DSC Onset was determined as 120 ± 0.3°C.

Example 10 (comparative example):

Injection molding was used to produce tensile specimens from the pellets from example 9. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured was s = 1385 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 7.8 kJ/m^2. Both tests were carried out at 23°C.

Example 11 (comparative example):

The pellets from example 9 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 45.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C. It was impossible to produce pipes suitable for the subsequent application. The pipes were not circular with respect to external diameter, and the wall thickness distribution was non-uniform. They did not comply with the requirements of DIN 8077 with respect to the dimensional limits for the average external diameters and the ovalities, and the dimensional limits for the wall thicknesses.

Example 14 (inventive):

Injection molding was used to produce tensile specimens from the pellets from example 13. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured at 23°C was s = 847 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 7.3 kJ/m^2.

Example 15 (inventive):

The pellets from example 13 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 800 × 45.3 mm (external diameter d_a = 800 mm, wall thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently, and the inner surface of the pipe was very smooth. The pipes had a satisfactory circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.2 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 46.6 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 47.9 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 48.3 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 47.2 mm
Test point 6	(sixty degrees distant	

tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured at 23°C was s = 871 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 6.4 kJ/m^2.

Example 18 (comparative example):

The pellets from example 16 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 800 × 45.3 mm (external diameter d_a = 800 mm, wall thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C. The processing was found to proceed very consistently.

The pipes had a circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.3 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 46.9 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 48.7 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 49.3 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 47.9 mm
Test point 6	(sixty degrees distant from 5 clockwise):	s_6 = 46.3 mm

evaporation.

This gave 10.6 kg of a propylene copolymer with 4.1% by weight of copolymerized ethylene. The catalyst yield calculated from these data is 30.6 kg of propylene copolymer/g of catalyst, i.e. titanium-containing solid component. The resultant propylene copolymer had a melt flow rate MFR of 1.10 g/min, a cold-xylene-soluble fraction of 4.0% by weight, and a polydispersity Mw/Mn of 10.3. The experiment was repeated a number of times in order to prepare a total amount of 500 kg.

Example 20 (comparative example):

The powder obtained from example 19 was pelletized at about 240°C under an inert gas in a twin-screw extruder with a screw diameter of 53 mm. Stabilizers added here were 0.15% of Irganox® 1010 and 0.15% of Hostanox® PAR 24. Color pigments were also added in order to adjust the color to RAL 7032. 0.2% of ultrafine talc (commercially available product from Luzenac) was added as nucleating agent. The MFR 230/5 measured on the pellets was 1.12 g/10 min. DSC Onset was determined as 107 ± 0.4°C.

Example 21 (comparative example):

Injection molding was used to produce tensile specimens from the pellets from example 20. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured at 23°C was s = 893 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength at 0°C to ISO 179/1eA. The a_{cn} value measured was 5.5 kJ/m^2.

Example 22 (comparative example):

The pellets from example 20 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 800 × 45.3 mm (external diameter d_a = 800 mm, wall thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

It was impossible to produce pipes suitable for the subsequent application. The pipes were not circular with respect to external diameter, and the wall thickness distribution was non-uniform. The pipes did not comply with the requirements of DIN 8077 with respect to dimensional limits for the average external diameters, and the ovalities, and the dimensional limits for the wall thicknesses. The inner surface of the pipes was very rough.

Injection molding was used to produce tensile specimens from the pellets from example 24. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens at 23°C. The value measured at 23°C was s = 1123 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength at 0°C to ISO 179/1eA. The a_{cn} value measured was 15.9 kJ/m^2.

Example 26 (inventive):

The pellets from example 24 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 5.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently, and the inner surface of the pipe was very smooth. The pipes had a satisfactory circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.3 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 46.4 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 47.5 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 48.6 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 47.5 mm
Test point 6	(sixty degrees distant from 5 clockwise):	s_6 = 46.2 mm

a_{cn} value measured was 11.6 kJ/m^2.

Example 29 (comparative example):

The pellets from example 27 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 45.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently. The pipes had a circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.2 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 47.6 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 49.0 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 49.7 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 48.6 mm
Test point 6	(sixty degrees distant from 5 clockwise):	s_6 = 47.2 mm

Roughness was measured on the inner surface of the pipe, which was very rough:

The following values were found:

titanium-containing solid component. The resultant propylene copolymer had a melt flow rate MFR of 1.16 g/min and a cold-xylene-soluble fraction of 11.0% by weight.

Example 31 (comparative example):

The powder obtained from example 30 was pelletized at about 240°C under an inert gas in a twin-screw extruder with a screw diameter of 53 mm. Stabilizers added here were 0.15% of Irganox® 1010 and 0.15% of Hostanox® PAR 24. Color pigments were also added in order to adjust the color to RAL 7032. 0.2% of ultrafine talc (product commercially available from Luzenac) were added as nucleating agent. The MFR 230/5 measured on the pellets was 1.16 g/10 min. DSC Onset was determined as 116 ± 0.2°C.

Example 32 (comparative example):

Injection molding was used to produce tensile specimens from the pellets from example 31. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured at 23°C was s = 1265 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength at 0°C to ISO 179/1eA. The a_{cn} value measured was 7.1 kJ/m^2.

Example 33 (comparative example):

The pellets from example 31 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 500 × 45.4 mm (external diameter d_a = 500 mm, wall thickness s = 45.4 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

It was impossible to produce pipes suitable for the subsequent application. The pipes were not circular with respect to external diameter, and the wall thickness distribution was non-uniform. The pipes did not comply with the requirements of DIN 8077 in relation to the dimensional limits for the average external diameters and the ovalities, and the dimensional limits for the wall thicknesses. The inner surface of the pipes was very rough.

No long-term internal-hydrostatic-pressure test was carried out.

The pipe was also subjected to a flexural impact test to DIN 8078 at 0°C and -10°C, using a nominal impact-pendulum energy of 15 J. The test specimens for this were taken from the pipe wall mechanically. The test was passed only at 0°C. The energy absorbed was 75 kJ/m^2 at 0°C,

The pellets from example 35 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 800 × 45.3 mm (external diameter d_a = 800 mm, wall thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently, and the inner surface of the pipe was very smooth. The pipes had a satisfactory circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes)..

Test point 1	(top of pipe):	s_1 = 45.4 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 46.2 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 47.6 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 48.6 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 47.4 mm
Test point 6	(sixty degrees distant from 5 clockwise):	s_6 = 46.5 mm

Roughness was measured on the inner surface of the pipe, which was very smooth:

The following values were found:

a)	maximum isolated roughness depth	R_{max}:	3.25 mm
b)	average roughness depth	R_z:	2.59 mm
c)	arithmetic mean roughness	R_a:	0.34 mm

thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

The processing was found to run very consistently. The pipes had a circular cross section. The dimensional limit for ovality to DIN 8077 was not exceeded.

Wall thickness was determined at six test points with sixty-degree separation around the pipe. For pipes of these dimensions to DIN 8077, the wall thickness has to be from s = 45.0 to s = 49.8 mm (the values given being averages measured on 3 pipes).

Test point 1	(top of pipe):	s_1 = 45.4 mm
Test point 2	(sixty degrees distant from 1 clockwise):	s_2 = 47.3 mm
Test point 3	(sixty degrees distant from 2 clockwise):	s_3 = 48.9 mm
Test point 4	(sixty degrees distant from 3 clockwise):	s_4 = 49.6 mm
Test point 5	(sixty degrees distant from 4 clockwise):	s_5 = 48.7 mm
Test point 6	(sixty degrees distant from 5 clockwise):	s_6 = 46.9 mm

Roughness was measured on the inner surface of the pipe, which was very rough:

The following values were found:

a)	maximum isolated roughness depth	R_{max}:	13.05 mm
b)	average roughness depth	R_z:	9.72 mm
c)	arithmetic mean roughness	R_a:	1.37 mm
d)	maximum roughness depth	R_t:	13.73 mm

The DIN 8078 long-term internal-hydrostatic-pressure test was carried out on the pipe:

Example 43 (comparative example):

Injection molding was used to produce tensile specimens from the pellets from example 42. A tensile test to ISO 527/1 + 2 to determine tensile modulus of elasticity was carried out on the tensile specimens. The value measured was s = 1404 MPa. The toughness of the molding composition was determined via the Charpy notched impact strength to ISO 179/1eA. The a_{cn} value measured was 7.2 kJ/m^2. Both tests were carried out at 23°C.

Example 44 (comparative example):

The pellets from example 42 were processed on an extrusion plant (screw diameter d_s = 90 mm, L/D = 30, grooved bush with thermal isolation, spiral-groove distributor, vacuum spray tank calibration), to give pipes of dimensions 800 × 45.3 mm (external diameter d_a = 800 mm, wall thickness s = 45.3 mm). The weight throughput was from 380 to 410 kg/h, depending on the take-off speed. The barrel temperatures were set so as to give a melt temperature of 215°C.

It was impossible to produce pipes suitable for the subsequent application. The pipes were not circular with respect to external diameter, and the wall thickness distribution was not uniform. The pipes did not comply with the requirements of DIN 8077 in relation to the dimensional limits for the average external diameters and the ovalities, and the dimensional limits for the wall thicknesses. The inner surface of the pipes was very rough.

No long-term internal-hydrostatic-pressure test was carried out.

The pipe was also subjected to a flexural impact test to DIN 8078 at 23°C and 15°C, using a nominal impact-pendulum energy of 15 J. The test specimens for this were taken from the pipe wall mechanically. The test was passed only at 23°C. The energy absorbed was 78 kJ/m^2 at 23°C, 53 kJ/m^2 at 15°C.

moldings.

13. The use of the molding compositions as claimed in any of claims 1 to 9 as materials for pipes.

14. A pipe obtained from the molding compositions as claimed in any of claims 1 to 9.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/14650

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/10 F16L9/12 C08L23/12 C08L23/14 C08F10/06 C08F210/06 C08K5/34
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K H16L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 03, 27 February 1998 (1998-02-27) & JP 9 291114 A (SHOWA DENKO KK), 11 November 1997 (1997-11-11) abstract -----	1,2,12
Y	EP 0 177 961 A (DANUBIA PETROCHEMIE) 16 April 1986 (1986-04-16) cited in the application the whole document -----	1-14
Y	EP 1 260 545 A (BOREALIS TECH OY) 27 November 2002 (2002-11-27) the whole document ----- -/--	1-14

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 April 2004	06/05/2004
Name and mailing address of the ISA	**Authorized officer**
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Droghetti, A

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/14650

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
JP 9291114	A	11-11-1997	NONE			
EP 0177961	A	16-04-1986	AT	381110	A	25-08-1986
			AT	322984	A	15-01-1986
			CS	8507292	A3	18-11-1992
			DE	3443599	A1	17-04-1986
			DE	3561399	D1	18-02-1988
			EP	0177961	A2	16-04-1986
			HU	40152	A2	28-11-1986
			SK	277920	B6	09-08-1995
EP 1260545	A	27-11-2002	EP	1260545	A1	27-11-2002
			WO	02094923	A1	28-11-2002
			EP	1399505	A1	24-03-2004
US 4138520	A	06-02-1979	JP	1175153	C	28-10-1983
			JP	52033954	A	15-03-1977
			JP	58001646	B	12-01-1983
			JP	1148987	C	26-05-1983
			JP	52035272	A	17-03-1977
			JP	57022736	B	14-05-1982
			JP	1175154	C	28-10-1983
			JP	52043868	A	06-04-1977
			JP	58001648	B	12-01-1983
			JP	51063500	A	01-06-1976
			JP	56011963	B	18-03-1981
			DE	2553693	A1	12-08-1976
			FI	753354	A ,B,	30-05-1976
			GB	1490454	A	02-11-1977
US 5962595	A	05-10-1999	DE	19621022	A1	27-11-1997
			AT	221098	T	15-08-2002
			AU	728337	B2	04-01-2001
			AU	2351597	A	27-11-1997
			BR	9703390	A	15-09-1998
			BR	9703396	A	15-09-1998
			CA	2205887	A1	24-11-1997
			CZ	9701603	A3	17-12-1997
			DE	59707768	D1	29-08-2002
			EP	0808870	A2	26-11-1997
			ES	2183041	T3	16-03-2003
			HU	9700935	A1	29-06-1998
			IL	120896	A	31-07-2003
			JP	10053628	A	24-02-1998
			NO	972371	A	25-11-1997
			PL	320157	A1	08-12-1997
			SK	65597	A3	11-06-1999
			TR	9700413	A2	21-12-1997
			TW	474948	B	01-02-2002
			ZA	9704516	A	24-11-1997